

Out-Life Characteristics of IM7/977-3 Composites

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ABSTRACT

The capability to manufacture large structures leads to weight savings and reduced risk relative to joining smaller components. However, manufacture of increasingly large composite components is pushing the out-time limits of epoxy/ carbon fiber prepreg. IM7/977-3 is an autoclave processable prepreg material, commonly used in aerospace structures. The out-time limit is reported as 30 days by the manufacturer. The purpose of this work was to evaluate the material processability and composite properties of 977-3 resin and IM7/977-3 prepreg that had been aged at room temperature for up to 60 days. The effects of room temperature aging on the thermal and visco-elastic properties of the materials were investigated. Neat resin was evaluated by differential scanning calorimetry to characterize thermal properties and change in activation energy of cure. Neat resin was also evaluated by rheometry to characterize its processability in composite fabrication. IM7/977-3 prepreg was evaluated by dynamic mechanical analysis to characterize the curing behavior. Prepreg tack was also evaluated over 60 days. The overall test results suggested that IM7/977-3 was a robust material that offered quality laminates throughout this aging process when processed by autoclave.

1. INTRODUCTION

The Ares V Cargo Launch vehicle is slated to utilize epoxy/carbon fiber composites in several dry structures; most of which are of substantial size. For example, the rocket interstage is planned to be 10 meters in diameter and 12 meters in height. It has been anticipated that processing these structures could push the out-life limits of most conventional carbon fiber/epoxy prepreg materials.

Many common epoxy systems used in the aerospace industry are composed of a mixture of epoxies, curing agent, and catalyst. Many times the curing agent is an amine, which reacts with the epoxy at room temperature. Consequently, prepreg material is kept frozen to avoid premature advancement of cure. This requirement raises concern for the fabrication of a large

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part where plies initially placed on a tool would be kept at room temperature until the remainder of the part is laid up. Cure advancement of the epoxy within those early plies could alter the rheology and cure profile of the material, and result in inhomogeneous cure in the overall laminate.[1] Additionally, loss of tack as the material sits on the tool may lead to voids or debonded area within the laminate.[2]

In this work, the processability and cure chemistry of IM7/977-3 was investigated with respect to the materials out-time. Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Rheometry were the primary characterization techniques. DSC has been widely used to characterize kinetic parameters of epoxy cure; as well as other resin systems.[3] Values such as activation energy, pre-exponential factor and rate constant can be obtained by either isothermal or dynamic experiments. Rheometry is widely used to measure the visco-elasticities of the curing resin and identify its processing window. DMA is an effective technique for prepreg process characterization. In-situ cure monitoring by this method has been used to identify processes such as gelation and vitrification.[4] Two to three ramp rates were used during these analyses and composite fabrications. This included a 0.28°C (0.5°F) per minute ramp rate, which is slow with respect to the manufacturers recommended ramp rate, but likely representative of the actual rate of temperature change within a large part during autoclave or oven cure.

2. MATERIALS

IM7/977-3 (145gsm, FAW) and 977-3 epoxy resin were received from Cytac Industries. Both materials were used within the manufacturers recommended freezer life period. Out-time samples were prepared by leaving prepreg or resin out of the freezer, at room temperature, but in a plastic Ziploc to avoid potential dust accumulation.

3. EXPERIMENTS

3.1 Differential Scanning Calorimetry (DSC)

A modulated Differential Scanning Calorimeter (DSC/Model No Q1000, TA Instruments) was used to evaluate the cure reaction enthalpy of the epoxy resin, thus the degree of cure advancement. The resin (8-12 mg) was weighed into a crimped aluminum DSC pan. The tests were performed under nitrogen, with the ramp rates including 0.5°C/min, 2°C/min, and 4°C/min. A second set of DSC tests were performed at ramp rates including 2.5°C/min, 5.0°C/min, and 10.0°C/min. Kinetic parameters such as activation energy (E_a) were calculated following ASTM E698-05.

3.2 Dynamic Mechanical Analyzer (DMA)

Additional processing characteristics, including modulus, gelation, and vitrification temperatures were obtained by Dynamic Mechanical Analysis (DMA/Model No 2980, TA Instruments). The

uncured prepreg was placed in a torsional holder and the experiment was run following the manufacturers cure cycle, with the exception that that ramp rate was modified to either 0.28°C/min (0.5°F/min) or 1.11°C/min (2°F/min).

3.3 Rheometer

Dynamic rheological measurements were conducted using a parallel-plate fixture on a rheometer (ARES, TA Instruments). The lower plate was oscillated at a fixed strain of 10% and a fixed angular frequency of 10 rad/sec while the upper plate was attached to a transducer which recorded the resultant torque. Fresh and out-time resin specimens were trimmed to disks of 2.54 cm in diameter, then loaded onto the rheometer between parallel plates and heated from RT to 177°C at 1°C/min. Storage (G') and loss (G'') moduli were obtained as a function of time (t) during the temperature ramp. These moduli were then converted to the complex viscosity $\eta^*(t)$. The specimen's softening point, the minimum viscosity and the gelation temperature and processing window were identified from the measurements.

3.4 Thermal Gravimetric Analysis (TGA)

TGA experiments (TA Instruments, Model Q500) were performed to characterize moisture absorption in the out-time resin. Resin was placed in the tared pan and temperature ramp of 10°C was used. The weight loss at 110°C was noted over 60 days at room temperature.

3.5 Ultrasonic Imaging of Laminate Panels

Ultrasonic testing of the samples was accomplished using an immersion scan system manufactured by UTEX Inc. Scans were conducted in a pulse-echo mode with a single 5MHz transducer acting as both the sender and receiver. C-scan images were generated for each sample based on the amplitude of the ultrasonic wave reflecting from the back surface of the sample. Data was collected at 0.5mm (.02 in.) in both directions.

3.6 Prepreg Tack Measurement

Tack tests of the fresh and out-lived candidate prepreg materials were performed to determine the level of prepreg tack through its ability to adhere to itself and to a vertical surface. The procedure, which follows Cessna Aircraft Company Specification CPTI003, calls for a corrosion resistant steel plate with a commercial 2D finish and a 1-inch diameter roller. The tests were to be performed at 70°F ± 10°F and 0-60% RH, using two: 3-inch by 1-inch prepreg specimens; where the 3-inch dimension was in the 0° direction. The out-life specimens were stored in an open plastic bag to expose them to ambient humidity and temperature levels. To test, one piece of the prepreg specimen was attached to the plate with light pressure using the roller. The backing was removed and the second strip was applied on top of the first one and tacked in a

similar manner. Finally, the backing from the second strip was removed and the plate was positioned vertically. The tack level was determined as follows:

- A. Tack level I — Low tack, prepreg is stiff and boardy.
- B. Tack level II — Dry but slight drape.
- C. Tack level III — Slight tack, sticks to itself but not to a vertical surface. Unable to adhere to the vertical tool surface for 30 minutes.
- D. Tack level IV — Good tack, prepreg sticks to itself and vertical tool. Adhered to the vertical tool surface for more than 30 minutes.
- E. Tack level V — Sticks to the hands or gloves but no resin transfer.
- F. Tack level VI — High tack, wet, and sloppy with resin transfer.

3.7 Flat Laminate Fabrication

Fresh prepreg was laid up as a $[0]_{32}$ unidirectional laminate. The prepreg stacks were then placed in a plastic Ziploc bag which was left open at room temperature for up to 60 days. Panels were processed in the autoclave after 0, 30, 45, and 60 days. The bagging sequence consisted of non-porous Teflon sheets on both sides of the laminate, followed by Kapton Film on both sides. The laminate stack was covered with 2 layers of glass fabric and bagged for processing. The purpose of the non-porous Teflon was to minimize resin flow out of the laminate during processing. The sides of the laminate were also blocked with a silicone tape, as shown in Figure 1; again to minimize resin loss.

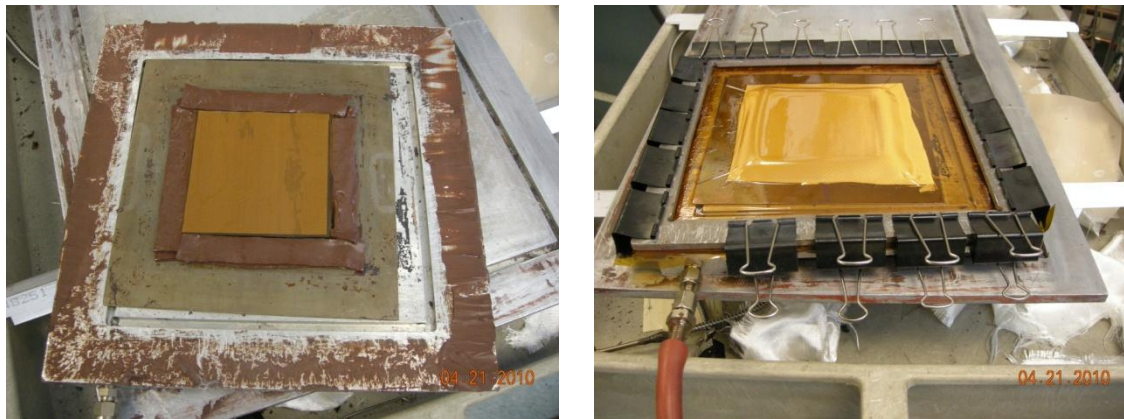


Figure 1: IM7/977-3 lay-up for autoclave processing.

Two ramp rates were used during processing; either 0.28 °C/min (0.5°F) or 1.11 °C/min (2.0°F). The cure profile used was:

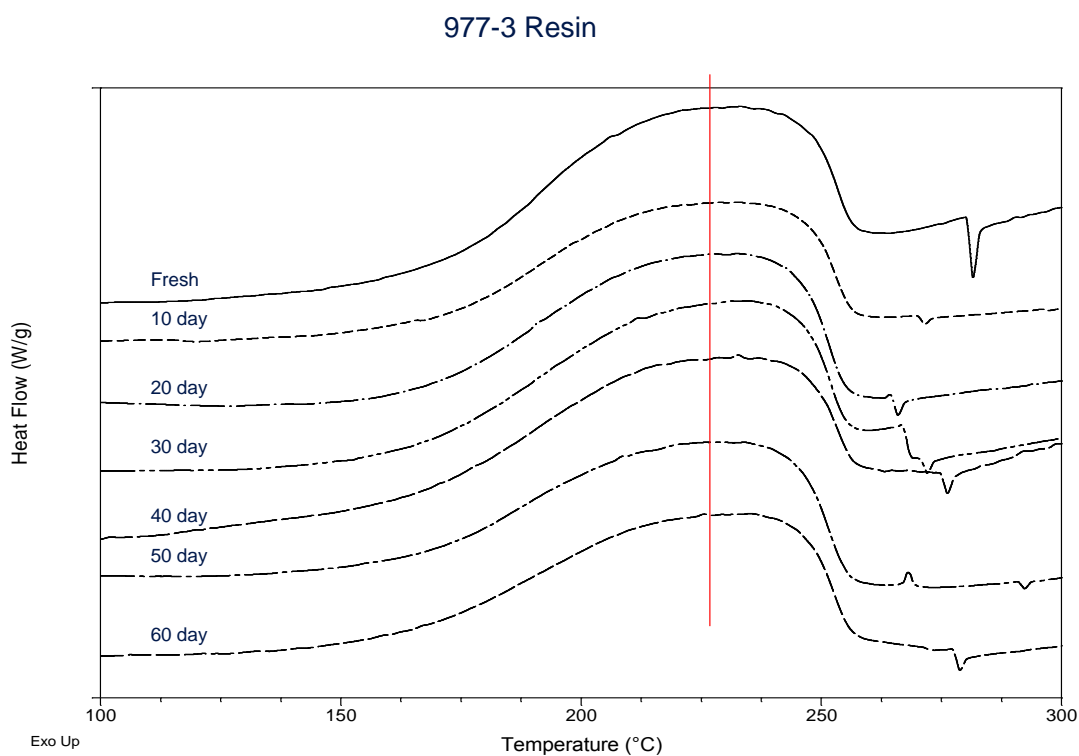
1. Bag panel and stabilize vacuum pressure at greater than 25 in Hg.
2. Apply 85 psi autoclave pressure and vent vacuum bag to atmosphere when pressure reaches 20 psig.
3. Heat to 177°C (350°F) at a rate of either 0.28 °C/min (0.5°F) or 1.11 °C/min (2.0°F)
4. Hold at 177°C (350°F) for 360 minutes.
5. Cool to 140°F at a rate of 1.5°F/min.
6. Release pressure.

4. RESULTS AND DISCUSSION

4.1 Resin Characterization

4.1a Results of DSC measurements

Sample DSC curves scanned at 2°C/min are shown in Figure 2. The heat of fusion during cure was calculated by integrating area under the exothermic peak. Results tabulated in Table 1 show some scatter in the enthalpy of the reaction with out-time, but no change in the temperature at which the peak reaction occurred. This scatter is likely due to error in precisely defining the onset of reaction. The absence of a significant decrease in enthalpy with out-time, and the consistency of the peak reaction temperature both suggest little to no room temperature conversion of the resin well beyond the manufacturer's recommended out-life. Furthermore, the resin maintained a 'gummy' nature for up to 50 days at room temperature, becoming gradually brittle beyond that time.



Figures 2: DSC curves of fresh and out-lifed 977-3 neat resins. Heated with 2 °C per min

Table 1. Thermal properties of 977-3 matrix resin

Out-time (day)	Heating rate (°C/min)	Onset reaction (°C)	Complete reaction (°C)	ΔH (J/g)	Peak exotherm (°C)
0	0.5	134	241	394	152
30		131	236	380	180
60		117	241	459	182
0	2	139	258	494	229
30		129	260	494	231
60		135	261	490	226
0	4	156	273	527	248
30		158	270	451	248
60		147	275	606	250
0	5	169	279	589	255
30		171	281	436	254
60		145	279	469	253
0	10	176	294	409	272
30		171	295	408	271
60		174	296	483	274

The measured enthalpy of cure as determined by the area under the exotherm in the DSC is plotted in Figure 3 and illustrates the stability of 977-3 resin to room temperature out-time.

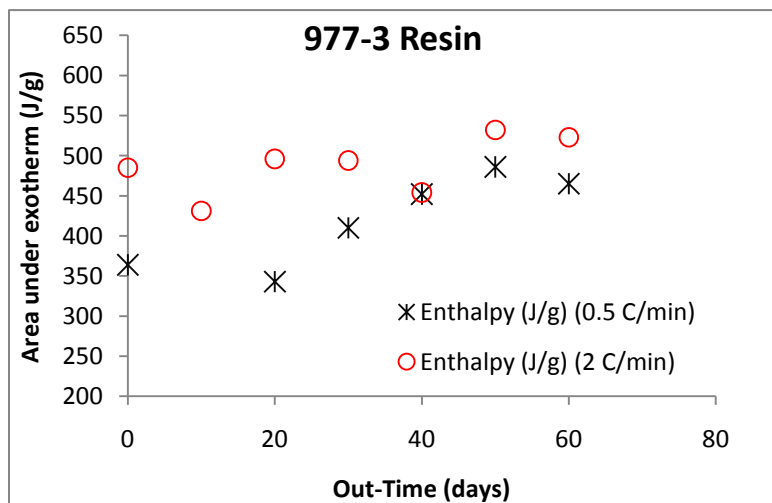


Figure 3: Plot of enthalpy of epoxy cure vs. resin out-time for 977-3 resin.

The moisture absorption into the resin was monitored with out-time and is listed in Table 2. Past work has demonstrated an increase in epoxy reaction rate following prepreg aging in a humidity chamber.[6] While moisture absorption did not appear to be a factor in the reactivity of aged 977-3, we did note an increase in weight loss at 110°C following extended out time at room temperature, which may be due to moisture absorption in the resin.

Table 2: Resin weight loss with increasing out-time as measured by TGA

Out-Time (days)	0	10	20	30	40	50	60
% wt loss (N₂) at 110 °C	0.15	0.23	0.27	0.22	0.29	0.3	0.37

DSC experiments of the 977-3 resin were initially run at three different heating rates; 0.5°C, 2°C, and 4°C per minute. These were chosen to approximate the ramp rate of composite processing. The cure kinetics of the resin were calculated from dynamic DSC experiments based on the Flynn/Wall/Ozawa method[7] which requires acquisition of three data points to calculate kinetic parameters including the activation energy of the cure reaction. However, the standard recommends ramp rates ranging between 2.5°C per minute and 10.0°C per minute, therefore a second set of DSC data was collected with ramp rates in this range. The E_a calculated based on data from the six DSC plots was stable over the 60 day out-time, as plotted in Figure 4. Stability of the activation energy implies there was limited conversion of the 977-3 resin during the 60 days at room temperature.

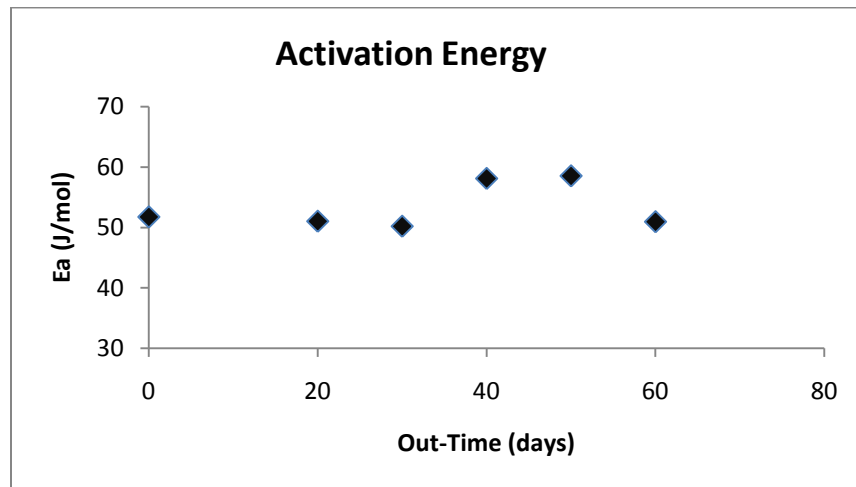


Figure 4: Activation energy of 977-3 resin from 0 to 60 days at room temperature.

The conversion of the fresh resin and the 60 day aged resin was calculated based on the equation:

$$\alpha = \Delta H_T / \Delta H_{\text{total}}$$

where α is conversion, ΔH_T is enthalpy at temperature T , and ΔH_{total} is the total heat of the cure reaction.(8) Percent conversion is plotted as a function of temperature in Figure 5, and shows no change in the conversion profile following 60 days out-time. The similarity between the two curves is indicative of (1) little to no advancement of the resin throughout aging and (2) no change is expected in the cure mechanism nor the chemical structure of the cured resin. (9)

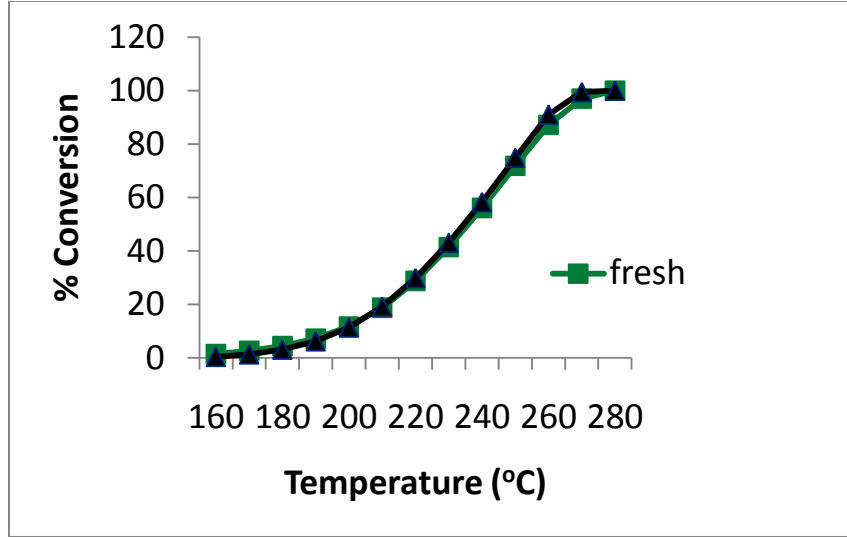


Figure 5: Percent conversion of 977-3 resin plotted as a function of temperature.

4.1b Rheometry Results

Figure 6 shows viscosity and $\tan \delta$ profiles during cure for fresh and 8-week out-time aged neat resins. The specimens were subjected to same temperature scan profile, i.e., $1^\circ\text{C}/\text{min}$ heating from RT to 177°C and hold for 30 mins. The curing characteristics are tabulated in Table 3. Fresh and out-timed resin specimens softened immediately upon heating and reached minimum viscosities of 30 P and 51 P, at 134°C and 142°C , respectively. Both viscosities were low, however, the out-timed resin exhibited a higher value. Superior processability of the 977-3 matrix resin was further evidenced by a rather wide temperature range (i.e., 40°C between 100 and 140 mins during temperature ramp in Figure 6) in which the viscosity value remained low and stable. Similar behavior was also observed for prepreg material measured by DMA in Figure 7, where storage modulus, E' , remained unchanged between 75 and 135 minutes (i.e., 111°C to 177°C , a range of 66°C).

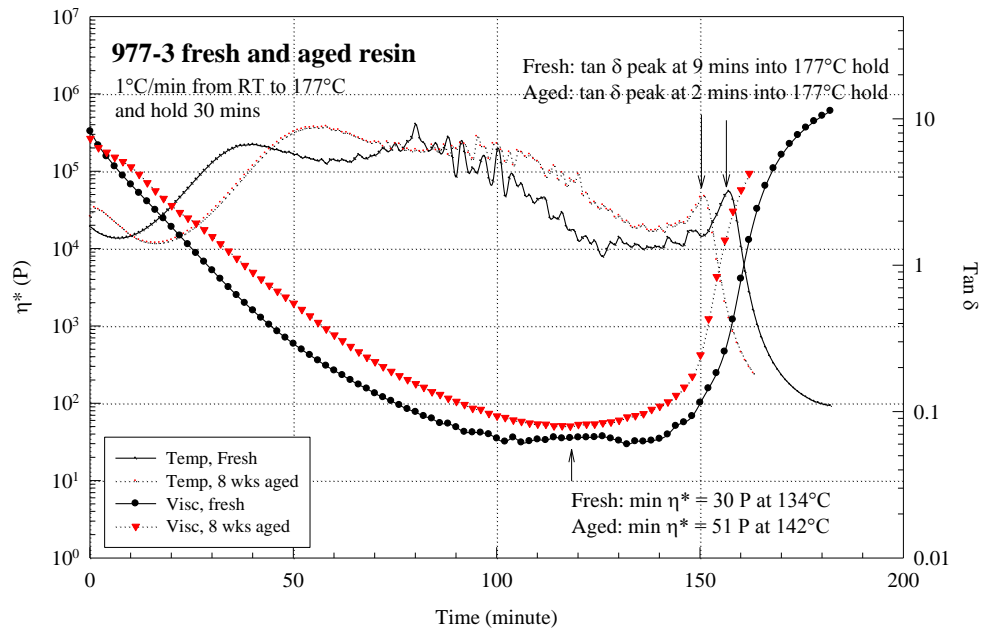


Figure 6: Viscosity and tan δ profiles of 977-3 fresh and 8-week out-time aged neat resins. Temperature scan rate 1°C/min from RT to 177°C and hold for 30 minutes.

Figure 6 suggests an earlier onset of cure for the out-time aged specimen as indicated by rising viscosities as temperatures increased. Peaks in tan δ profiles are listed in Table 3 for both fresh and aged specimens. Also tabulated in Table 3 are the temperatures and times in which tan $\delta = 1$ occurred. These two transition points are commonly used to define its gelation point during resin cure. In both cases, it was noted that the aged specimen gelled only 6-7 mins earlier than the fresh specimen. This suggests that the 8-week out-time aged resin suffered a minimal advancement in resin curing reaction and processability of composite prepregs.

Table 3. Curing characteristics of fresh and out-timed 977-3 matrix resins from rheometer measurements at 1°C/min heating scan

Specimen ID	Minimum Viscosity		Peak tan δ occurred	tan $\delta = 1$ occurred
	Value (P)	at Temp (°C)		
Fresh	30	134	at 8 mins into 177°C hold	at 12 mins into 177°C hold
8-week out-time	51	142	at 2 mins into 177°C hold	at 5 mins into 177°C hold

4.2 Prepreg Characterization

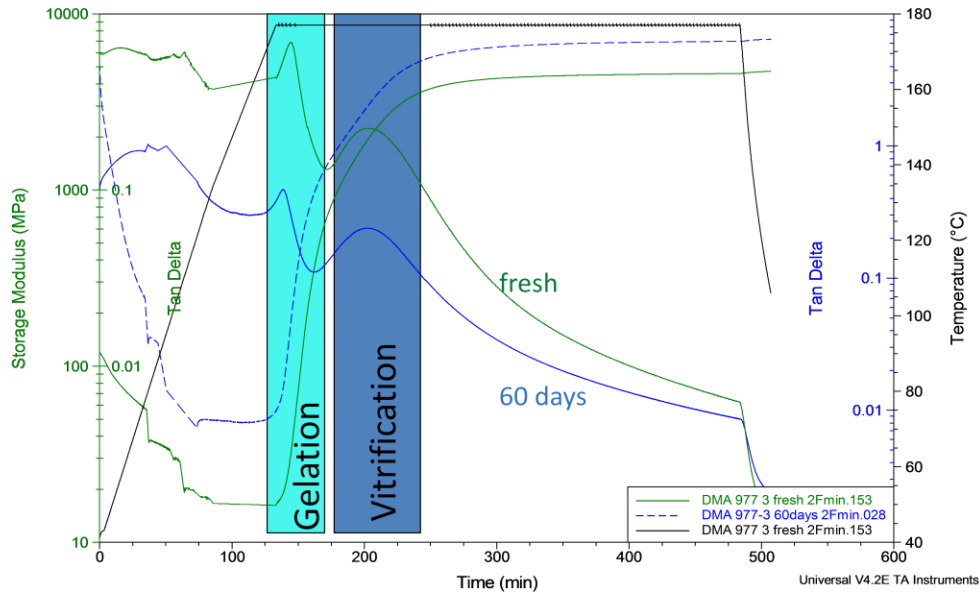
4.2a Results of DMA measurements

The temperature profile used in the dynamic mechanical analysis experiments followed the manufacturers recommended cure profile, except for the heating rate which was either 0.28 °C (0.5 °F) or 1.11 °C (2 °F) per minute. Therefore, the profile of the DMA experiment included a ramp to 177°C, followed by a 6 hour hold at that cure temperature. Two variables were studied in this experiment including ramp rate and prepreg out-time. Variation of ramp rate did not change the shape of the curve but shifted both storage modulus, E' , and $\tan \delta$ curves with respect to the hold temperature in the cure cycle.

- Figure 7 shows the E' vs. time scan (at the 1.11°C per minute ramp rate) of the fresh and 60 day out, uncured, epoxy prepreg. The plots show a reduction in E' at the onset of the experiment which is related to softening of the matrix on heating from room temperature. The mixture remains at a reduced E' until the hold temperature is reached in the cure profile (135 min, 177°C). At this time, the storage modulus begins to rise. Two peaks occur in the $\tan \delta$ plot; the first peak maximum occurs at 145 minutes and appears to indicate the onset of gelation, and the second at 200 minutes would be indicative of vitrification.[10]
- There was a considerable reduction in the onset temperature of cure at the slower cure rate, 0.28°C per minute. The temperature scan also shows an early reduction in E' at the onset of the experiment due to softening of the matrix. However, at this ramp rate, the modulus begins to build at 155 °C, which is more than 20 °C earlier than the 1.11 °C/min rate. $\tan \delta$ peaks related to gelation and vitrification occur at 163 °C and 177 °C, respectively.

The vitrification peak does not necessarily mark the end of network formation, rather it indicates that the resin glass transition temperature, T_g , has reached the cure temperature. As a result, the T_g of the isothermally cured resin will be higher than the cure temperature. It is important to note that the peak associated with vitrification occurs at 177 °C at both ramp rates. The primary difference was that the 0.28 °C per minute ramp led to vitrification at the onset of the isothermal hold, whereas at the faster ramp, vitrification was reached over an hour into the isothermal hold.

A summary of the cure, gelation, and vitrification temperatures is given in Table 4. As with DSC, the DMA results showed little variation in prepreg behavior with out-time up to 60 days.



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Figure 7: Dynamic Mechanical Analysis plots of IM7/977-3 prepreps following 0 and 60 days out-times at 1.11 °C/min ramp rate.

Table 4. Curing characteristics of fresh and out-timed IM7/977-3 prepreps from DMA measurements at 1.11°C/min heating scan

Sample ID	Onset of Cure (X min into 350 °F (177 °C) hold)	First tan d peak (X min into 350 °F (177 °C) hold)	Second tan d peak (X min into 350 °F (177 °C) hold)
2°F per min ramp			
Fresh	0 min Temp = 177 °C	10 min Temp = 177 °C	70 min Temp = 177 °C
60 days	0 Temp = 177 °C	15 min Temp = 177 °C	80 min Temp = 177 °C
0.5°F per min ramp			
Fresh	-100 min Temp = 153 °C	-50 min Temp = 163 °C	40 min Temp = 177 °C
55 days (due to ID of onset of cure in 60 day plot)	-120 min Temp = 150 °C	-80 min Temp = 155 °C	20 min Temp = 177 °C

4.2b Prepreg Tack Measurements:

The tack test results are summarized in Table 5 below and shows that IM7/977-3 prepreg retained tack and some drape through 60 days out-time at room temperature.

Table 5. Qualification of prepreg tack with out-time.

Material	Out-Time/ Tack Level				
	0 days	15 days	30 days	45 days	60 days
IM7/977-3	V	IV	IV	IV	III

4.3 Out-time effects on cured laminate panel quality

Quality of the cured laminates was examined by ultrasonic imaging, and shown in Figures 8-10. The results showed better consolidation in the 45 day processed material than the 0 or 30 day. This was not material related, but low vacuum and low pressure issues while processing the 0 and 30 day panels. In addition, the panels slated to be processed at 60 days were processed at 62 days 1.11°C/min (2°F/min) and 67 days 0.28°C/min (0.5°F/min) due to autoclave maintenance.

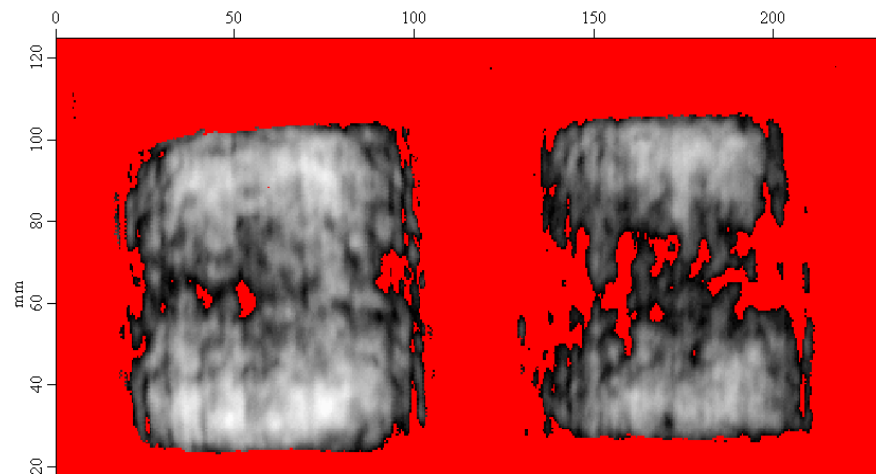


Figure 8: Panels cured after 0 days (left) and 30 days (right) at RT; ramp rate was 1.11°C/min

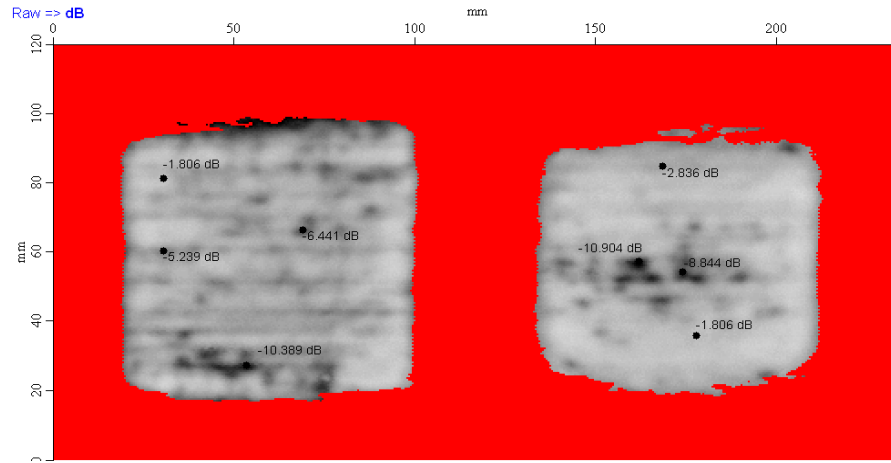


Figure 9: Panels cured after 45 days at RT, ramp rate = $-.28^{\circ}\text{C}/\text{min}$ (left) and $1.11^{\circ}\text{C}/\text{min}$ (right)

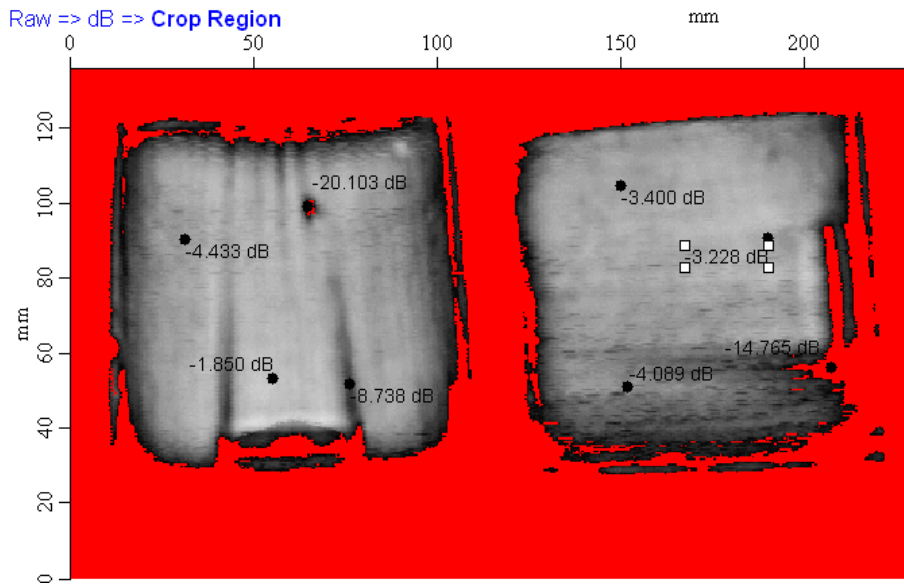


Figure 10: Panels cured after 67 days at RT, $0.28^{\circ}\text{C}/\text{min}$ (left) and 62 days, ramp rate of $1.11^{\circ}\text{C}/\text{min}$.

Unfortunately, quality laminates were not obtained with the fresh material for comparison. The attenuation loss noted on each panel shows slight loss of quality in the composites processed beyond 60 days, relative to the 45 day panels.

5. CONCLUSIONS

DSC and DMA analyses demonstrated that IM7/977-3 offered minimal cure advancement of the resin when left at room temperature for up to 60 days. DSC of the resin showed no change in the enthalpy of the crosslinking reaction with aging, or in the temperature at which the epoxy cure process occurs. Rheology studies of the resin support the DSC data and show minimal change in the resin viscosity profile with out-time. DMA studies of the prepreg material showed similar

stability with out-time. The DMA plots did however show a reduction in gelation and vitrification temperatures as the ramp rate was reduced from 1.11°C to 0.28°C. A high level of resin tack was maintained through 45 days of aging at room temperature.

6. REFERENCES

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